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#### **PCT**

#### **NOTIFICATION OF ELECTION**

(PCT Rule 61.2)

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Applicant's or agent's file reference

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Applicant

BAYENSE, Cornelis, Roeland et al

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The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland

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RIFLACED BY 00/25918 order to minimise pressure drop, the use of star shaped extrudates would be most suitable. However, star shaped bodies, extrudates, tend to be prone to attrition due to the

presence of the 'points' of the star.

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It is an object of the invention to reconcile these various requirements in the form of a transition alumina extrudate, having a carefully balanced set of properties. Further objects and advantages will become clear from the following description of the invention and the preferred embodiments thereof.

The invention is based thereon that the inventors have now been able to provide a star shaped alumina extrudate, having on the one hand an optimal structure, as indicated above and on the other hand a good strength.

The invention is accordingly directed to star shaped alumina extrudates with a pore volume in pores of diameter of over 1000 nm, as determined by mercury porosimetry, of at least 0.05 ml/g, a side crushing strength of at least 50 N and a bulk crushing strength of at least 1 MPa.

Surprisingly, this set of properties can be made available in one material, thereby providing a material with which chemical reactions can be made much more efficient, resulting in higher activity and/or selectivity. Also the material of the invention, when used in fixed bed reactors, provides a decreased pressure drop compared to regular extrudates having a cylindrical shape.

The BET surface area, as determined by single point adsorption using the BET equation (as e.g. described by G. Sandstede et.al., Chem. Ing. Tech. 32 (1960), 413), should be at least  $10 \text{ m}^2/\text{g}$  of alumina. This coincides with the requirement of using a transition alumina, i.e. not an  $\alpha$  alumina. Suitable alumina's are the various transition alumina's including  $\gamma$ -alumina,  $\delta$ -alumina,  $\epsilon$ -alumina,  $\kappa$ alumina,  $\zeta$ -alumina,  $\theta$ -alumina and  $\tau$ -alumina. These alumina's have a large BET-surface area, generally in the range of 25 up to more than  $100 \text{ m}^2/\text{g}$ .

# **PCT**



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

| Applicant's or agent's file reference   |  |  |
|---|--|--|
| P22013PC00  |  | ification of Transmittal of International<br>ary Examination Report (Form PCT/IPEA/416)  |
| International application No.   | International filing date (day/month/year)   | T  |
| PCT/NL99/00676  | 04/11/1999   | Priority date (day/month/year) 04/11/1998  |
| International Patent Classification (IPC) or nati                                 |  | 04/11/1990   |
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| Applicant   |  | <del></del>  |
| ENGELHARD CORPORATION, ET   | Δ1   |  |
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| This international preliminary examir and is transmitted to the applicant action. | nation report has been prepared by this Ir   | nternational Preliminary Examining Authority   |
| and is transmitted to the applicant at  | ocording to Article 36.  |  |
| 2. This PEPOPT consists of a total of   | Cahanta including this government  |  |
| 2. This REPORT consists of a total of   | 6 sneets, including this cover sneet.  |  |
| □ This report is also accompanied   | by ANNEXES, i.e. sheets of the descript  | tion, claims and/or drawings which have  |
| been amended and are the basi   | is for this report and/or sheets containing 7 of the Administrative Instructions under | rectifications made before this Authority  |
| (See Fidle 70. TO and Section 50  | 7 Of the Administrative monuctions under   | r the PC1).  |
| These annexes consist of a total of   | 1 sheets.  |  |
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|   |  |  |
| This report contains indications relations  | ing to the following items:  |  |
| _   | ing to the renorming name.   |  |
| I ⊠ Basis of the report   |  |  |
| II U Priority   |  |  |
| III  ☐ Non-establishment of op IV ☐ Lack of unity of invention                    | pinion with regard to novelty, inventive ste   | ep and industrial applicability  |
|   | der Article 35(2) with regard to novelty, in   | ventive step or industrial applicability:  |
| citations and explanation   | ns suporting such statement  | rective step of madelia, applicability,  |
| VI  |  |  |
| VII  Certain defects in the int   | • •  |  |
| VIII U Certain observations on  | the international application  | 4  |
|   |  |  |
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| Date of submission of the demand  | Date of completion   | of this report   |
| 21/05/2000  | 17.01.2001   |  |
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|   | <del></del>  |  |
| Name and mailing address of the international                                     | Authorized officer   | ALSOVES MICE.  |
| preliminary examining authority:  | Authorized officer   | ST S   |
|   | de Cauwer, B   | Company of the second s |

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL99/00676

#### I. Basis of the report

| 1. | res<br>the | sponse to an invitati                               | on under Article 14 are i                              | ubstitute sheets which have been furnished to the receiving Office in<br>referred to in this report as "originally filed" and are not annexed to<br>nts (Rules 70.16 and 70.17).): |
|----|------------|---|--|--|
|    | 1,3        | 3-6   | as originally filed                                    |  |
|    | 2          |   | with telefax of  | 24/11/2000   |
|    | Cla        | aims, No.:  |  |  |
|    | 1-9        | )   | as originally filed                                    |  |
|    | Dra        | awings, sheets:                                     |  | ·  |
|    | 1/1        |   | as originally filed                                    |  |
|    |            |   |  |  |
| 2. | Wit<br>lan | h regard to the <b>lang</b><br>guage in which the i | guage, all the elements r<br>international application | narked above were available or furnished to this Authority in the was filed, unless otherwise indicated under this item.   |
|    | The        | ese elements were a                                 | available or furnished to                              | this Authority in the following language: , which is:  |
|    |            | the language of a                                   | translation furnished for                              | the purposes of the international search (under Rule 23.1(b)).   |
|    |            | the language of pu                                  | ublication of the internati                            | onal application (under Rule 48.3(b)).   |
|    |            | the language of a 55.2 and/or 55.3).                | translation furnished for                              | the purposes of international preliminary examination (under Rule  |
| 3. | Wit        | h regard to any <b>nuc</b><br>rnational preliminar  | eleotide and/or amino a<br>y examination was carri     | cid sequence disclosed in the international application, the ed out on the basis of the sequence listing:  |
|    |            | contained in the in                                 | ternational application in                             | written form.  |
|    |            | filed together with                                 | the international applica                              | tion in computer readable form.  |
|    |            | furnished subsequ                                   | ently to this Authority in                             | written form.  |
|    |            | furnished subsequ                                   | ently to this Authority in                             | computer readable form.  |
|    |            | The statement that the international ap             | t the subsequently furnis                              | shed written sequence listing does not go beyond the disclosure in en furnished.   |
|    |            |   | t the information recorde                              | d in computer readable form is identical to the written sequence   |
| 4. | The        | amendments have                                     | resulted in the cancella                               | tion of:   |

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL99/00676

|    |      | the description,                          | pages:                 |                          |   |
|----|------|---|------------------------|--------------------------|---|
|    |      | the claims,                               | Nos.:                  |                          |   |
|    |      | the drawings,                             | sheets:                |                          |   |
| 5. |      | This report has been considered to go bey | establishe             | ed as if (s<br>isclosure | ome of) the amendments had not been made, since they have beer as filed (Rule 70.2(c)): |
|    |      | (Any replacement shi<br>report.)          | eet contail            | ning such                | amendments must be referred to under item 1 and annexed to this                         |
| 6. | Add  | itional observations, if                  | necessar               | y:                       |   |
| V. | Rea  | soned statement un                        | der Artick<br>ns suppo | e 35(2) w<br>rting suc   | ith regard to novelty, inventive step or industrial applicability;                      |
| 1. | Stat | ement                                     |                        |                          |   |
|    | Nov  | elty (N)                                  | Yes:<br>No:            | Claims<br>Claims         | 1-9   |
|    | Inve | ntive step (IS)                           | Yes:<br>No:            | Claims<br>Claims         | 1-9   |
|    | Indu | strial applicability (IA)                 | Yes:<br>No:            | Claims<br>Claims         | 1-9   |
| 2. |      | tions and explanations<br>separate sheet  | 6                      |                          |   |

# VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted: see separate sheet

### **EXAMINATION REPORT - SEPARATE SHEET**

#### Re Item V

Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Claim 1 - Novelty

Claim 1 is a product claim for star shaped alumina extrudates with a pore volume of at least 0.05 ml/g in the pores with a diameter of over 1000 nm, a side crushing strength of at least 50 N and a bulk crushing strength of at least 1 MPa.

EP-A-0 008 424 (BASF AG) 5 March 1980 (1980-03-05), D1,

is regarded as being the closest prior art to the subject-matter of claim 1 and discloses (the references in parentheses applying to this document): star shaped extrudates (page 5, line 26-29) made from Al<sub>2</sub>O<sub>3</sub> (page 5, line 24) having a pore volume between 0.4 and 0.8 ml/g (page 5, line 5) with a high mechanical stability (page 4, line 22) and a pressure resistance of 10 kg (page 6, line 20).

The subject-matter of claim 1 therefore differs from that known in D1 in that the catalyst has a pore volume of at least 0.05 ml/g in the pores with a diameter of over 1000 nm. Although D1 states that the majority of the pores should be between 5 and 20 mm, this is obviously an error since this implies that the pores should be larger than the particles (examples page 6).

The subject-matter of claim 1 is therefore novel (Article 33 (2) PCT).

#### Claim 1 - Inventive step

The problem to be solved by the present invention is to provide a product that has a high mechanical strength and to eliminate diffusion limitation problems as much as possible.

The solution to this problem proposed in the present application is to provide a product with a pore volume of at least 0.05 ml/g in the pores with a diameter of over 1000 nm. This solution cannot be considered as involving an inventive step (Article 33 (3) PCT) since D1 solves the same technical problems as the current application, notably the provision of a product with a good mechanical stability (page 4, line 23) and a high activity, which obviously only can be achieved if there are no real problems of diffusion limitation. Furthermore no evidence has been given that the current product has any

**EXAMINATION REPORT - SEPARATE SHEET** 

advantage over the product of D1. Moreover, it is not unreasonable to assume that the pore volume in pores of diameter of over 1000 nm in the product of D1 is at least 0.05 ml/g, since this is only about 10% of the total pore volume of the product of D1 as well as in the current product. As a result it cannot be seen how the current product may be advantageous over the product of D1 and no inventive step can be recognised.

#### Claim 2 - 6 - Novelty & Inventive Step

Since the subject-matter of claim 1 is novel, that of the dependent claims 2 - 6 is novel too (Article 33 (2) PCT).

With regard to the inventive step, the same reasoning as for claim 1 applies and thus, the subject-matter of claims 2 - 6 is not inventive (Article 33 (3) PCT).

#### Claim 7 - Novelty & Inventive Step

Claim 7 is a product claim for a catalyst comprising at least one catalytically active material supported on an extrudate according to claims 1 - 6.

D1 discloses that the extrudate can be impregnated with a cobalt-nitrate solution (page 5, line 34).

Since the product of claim 1 is novel, the product of claim 7 can be regarded as novel too (Article 33 (2) PCT).

Since the problem to be solved is the same as for claim 1, the same reasoning applies as for claim 1, and thus, the subject-matter of claim 7 is not inventive (Article 33 (3) PCT).

#### Claim 8 - Novelty & Inventive Step

D1 further discloses that the catalytically active material can be cobalt (page 5, line 34). For these reasons and because claim 8 is dependent on claim 7, the subject-matter of claim 8 can be regarded as novel but not inventive (Article 33 (2) & (3) PCT).

#### Claim 9 - Novelty & Inventive Step

Claim 9 is a use claim of the products of claim 1 to 8 in a chemical reaction. The use of a novel product has to be considered novel too (Article 33 (2) PCT).

# INTERNATIONAL PRELIMINARY

International application No. PCT/NL99/00676

**EXAMINATION REPORT - SEPARATE SHEET** 

D1 discloses the use of the catalyst for hydrogenation reactions (claim 1, line 2). Thus, the subject-matter of claim 9 cannot be considered inventive (Article 33 (3) PCT).

#### Re Item VII

### Certain defects in the international application

To meet the requirements of Rule 5.1 a) ii) PCT, the document D1 should be identified in the description and the correct relevant background art disclosed therein should be briefly discussed.

#### Re Item VIII

### Certain observations on the international application

The subject-matter of claim 9 is considered unclear (Article 6 PCT) since it refers to the use of two different products.

# INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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A1

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**Published** 

With international search report.

(54) Title: STAR SHAPED ALUMINA EXTRUDATES AND CATALYST BASED THEREON

(57) Abstract

This invention is directed to star shaped alumina extrudates with a pore volume in the pores of a diameter over 1000 nm, as determined by mercury porosity, of at least 0.05 ml/g and a total pore volume between 0.5-0.75 ml/g. The extrudates have a length of between 2-8 mm, a length to diameter ratio of between 1-3, a side crushing strength of at least 50 N and a bulk crushing strength of at least 1 MPa.

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Title: STAR SHAPED ALUMINA EXTRUDATES AND CATALYST BASED THEREON

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The invention is directed to transition alumina extrudates, suitable as catalyst, or as catalyst support, and the use of such extrudates in chemical reactions.

In catalysis alumina plays an important role, both as a catalyst support and as catalytically active material. As is mentioned in Kirk-Othmer, Third Ed, Vol. 2, pages 230-232, alumina can be used as catalyst in a Claus process, for dehydration of alcohols, such as the production of olefins from alcohol, and the reverse reaction, but also for the isomerisation of olefins. As interacting catalyst support alumina may play a role in hydrorefining catalysts, e.g. in cobalt or nickel-molybdenum oxides on alumina.

As a support alumina is frequently used for precious metal catalyst, such as in exhaust catalysts or for (de)hydrogenation reactions. As support for a nickel catalyst it may be used in(de)hydrogenation reactions such as for fat and oils hydrogenation, for hydrogenation of fatty nitriles or of nitro aromatic compounds or for oligomerisation of olefins.

The structure of the support, i.e. the BET surface area, the pore size and the pore volume distribution, forms an important aspect of the alumina or alumina based catalyst. In view of activity and selectivity it would be highly desirable to have an alumina product that is on the one hand highly porous, i.e. having a large volume in large pores, and that has a good mechanical strength and stability. Unfortunately these are requirements that are difficult to reconcile with each other.

In fixed bed processes shaped bodies of alumina are frequently used. An important aspect therein is the shape dependency of the pressure drop. Tablets and extrudates are the materials commonly used in fixed bed applications. In

order to minimise pressure drop, the use of star shaped extrudates would be most suitable. However, star shaped bodies, extrudates, tend to be prone to attrition due to the presence of the 'points' of the star.

It is an object of the invention to reconcile these various requirements in the form of a transition alumina extrudate, having a carefully balanced set of properties. Further objects and advantages will become clear from the following description of the invention and the preferred embodiments thereof.

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The invention is based thereon that the inventors have now been able to provide a star shaped alumina extrudate, having on the one hand an optimal structure, as indicated above and on the other hand a good strength.

The invention is accordingly directed to star shaped alumina extrudates with a pore volume in pores of diameter of over 1000 nm, as determined by mercury porosimetry, of at least 0.05 ml/g, a side crushing strength of at least 50 N and a bulk crushing strength of at least 1 MPa.

Surprisingly, this set of properties can be made available in one material, thereby providing a material with which chemical reactions can be made much more efficient, resulting in higher activity and/or selectivity. Also the material of the invention, when used in fixed bed reactors, provides a decreased pressure drop compared to regular extrudates having a cylindrical shape.

The BET surface area, as determined by single point adsorption using the BET equation (as e.g. described by G. Sandstede et.al., Chem. Ing. Tech. 32 (1960), 413), should be at least 10 m²/g of alumina. This coincides with the requirement of using a transition alumina, i.e. not an  $\alpha$  alumina. Suitable alumina's are the various transition alumina's including  $\gamma$ -alumina,  $\delta$ -alumina,  $\epsilon$ -alumina,  $\kappa$ -alumina,  $\zeta$ -alumina,  $\theta$ -alumina and  $\tau$ -alumina. These alumina's have a large BET-surface area, generally in the range of 25 up to more than 100 m²/g.

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The pore volume is a further important requirement, whereby it is on the one hand important that the total pore volume, as determined by mercury intrusion is sufficiently high and on the other hand that the pore volume in pores of over 1000 nm forms a substantial portion of the total pore volume. In absolute terms the total pore volume should be at least 0.50 ml/g, whereas the ratio of the pore volume in pores of over 1000 nm to total pore volume should preferably be more than 0.04. An alumina having those properties has good properties in terms of reactant accessibility, which makes it very suitable for all kinds of catalytic reactions requiring good diffusion of reactants and products through the alumina, thereby eliminating diffusion limitation problems as much as possible.

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The pore volume and pore size distribution are determined by mercury porosimetry measurements, as described by J. Rouquerol et al in Pure & Applied Chem., 66(8),1994, pages 1752-1753, using the Washburn equation.

As indicated above, the use of star shaped extrudates is important in terms of pressure drop in relation to accessibility of the internal surface of the alumina. This also plays a role in eliminating diffusion problems. Star shaped extrudates can be defined as objects having some kind of central part or core, with three or more triangularly shaped extensions on the circumference thereof. Most preferred are star shaped extrusions having five extensions, as this provides the optimal balance between strength, porosity, pressure drop and accessibility. Another advantageous property of the star shaped extrudates is the fact that the ratio of external surface area to volume is more advantageous than in the case of conventional cylindrical extrudates or tablets.

The ratio of the length of the extrudates to the diameter is preferably between 1 and 3, whereby as diameter the distance is meant between two parallel planes on either side of the extrudate.

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Important aspects of the material of the invention are also the strength characteristics. As indicated above a side crushing strength of at least 50 N and a bulk crushing strength of at least 1 MPa are essential herein. These parameters form the basis for the suitability of the extrudates for use in large scale reactors, like in the petroleum industry. When the extrudates meet these requirements, they can be used in huge fixed bed reactors, that require very strong material. The side crushing strength and the bulk crushing strength is defined as follows:

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The side crushing strength (SCS) of extrudates is defined as the pressure (in Newtons) at which extrudates of 4.5-5.00 mm length are crushed, when treated under pressure between two flat plates on a AIKOH, 9500 series tester.

The bulk crushing strength (BCS) of a catalyst is defined as the pressure (in Megapascals) at wich 0.5% fines (i.e. particles less than 0.425 mm) are formed when treated under a piston in a tube. For that purpose, 17 ml of catalyst particles, presieved on a 0.425 mm sieve, are loaded in a cylindrical sample tube (diameter 27.3 mm), and 8 ml steel beads is loaded on top. The catalyst is subsequently treated at different (increasing) pressures for three minutes, after which the fines are recovered and their percentages is determined. This procedure is repeated until a level of 0.5 wt.% fines is reached.

Another aspect of the strength of the material is the attrition, i.e. the amount of material that may break off of the extrudates upon use. This attrition, determined in accordance with ASTM D4058-87, should preferably be less than 5 wt.%, more in particular less than 3 wt.%.

The alumina extrudates having the above properties can be prepared by mixing transition alumina powder with a suitable binder in the presence of a liquid, usually water or an aqueous solution of a mineral acid such as hydrochloric, sulfonic or nitric acid, to form a paste, followed by extruding of the paste in the required star form, using a

suitable die and cutting the extruded strands of material to the required length. Optionally after drying, the extrudates are calcined.

It is possible to use various types of binder materials, such as those based on silica or alumina. Examples are colloidal silica, waterglass, or clays. It is preferred to use an alumina based binder or a binder that is removed during calcination, while providing and maintaining the required strength. An example of a suitable binder system is an alumina binder that gels under acidic treatment, for example by using organic or inorganic acids. The amount of binder material used in the preparation of the paste that is to be extruded will vary depending on the type of material and the required strength. Generally it will not be in excess of 30 wt.% based on the dry weight of binder and alumina together.

The invention will now be elucidated on the basis of an example.

#### **EXAMPLE**

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1.5kg of aluminium trihydrate, containing 65 wt.% of  $Al_2O_3$ , with an average particle size of 30-50  $\mu m$  is mixed with 0.4 kg of alumina binder. The powders are mixed extensively while slowly adding diluted, aqueous HNO<sub>3</sub> in an amount of 2 wt.%, calculated on the weight of the total amount of alumina.

Thereby the alumina binder is peptised. Mixing is continued until a relatively dry product is obtained. the intermediate product is extruded using a one-screw extruder, equipped with a die having starshaped holes and a cutting device.

The extrudates obtained are dried at 105°C for 16 hours and subsequently calcined at 850°C for one hour. Attached are two figures with photographs of an extrudate shown from two different angles.

The final product has been analysed for its physical properties with the following result:

N<sub>2</sub>-BET surface area 106 m/g<sup>2</sup>

Total Hg pore volume 0.56 ml/g

Pore volume in pores over 1000 nm 0.07 ml/g

Side crushing strength 65 N

Bulk crushing strength 1.08 MPa

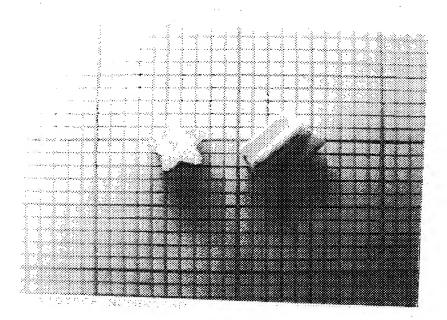
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1-6.

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#### Claims

- 1. Star shaped alumina extrudates with a pore volume in pores of diameter of over 1000 nm, as determined by mercury porosimetry, of at least 0.05 ml/g, a side crushing strength of at least 50 N and a bulk crushing strength of at least 1 MPa.
- 2. Extrudates according to claim 1, having a length of between 2 and 8mm.
- 3. Extrudates according to claim 1 or 2, having a length to diameter ratio of between 1 and 3.
- 10 4. Extrudates according to claims 1-3, wherein the total pore volume a determined by mercury porosimetry is between 0.5 and 0.75 ml/g.
  - 5. Extrudates according to claims 1-4, wherein the BET surface area is at least  $75 \text{ m}^2/\text{g}$ .
- 6. Extrudates according to claims 1-5, wherein the attrition in accordance with ASTM D4058-87 is less than 5 wt.%, preferably less than 3 wt.%.
  - 7. Catalyst, comprising at least one catalytically active material supported on an extrudate according to claims
  - 8. Catalyst according to claim 7, wherein the catalytically active material is selected from the group of metals, metal oxides, metal sulfides and combinations thereof.
- 9. Use of an extrudate according to claims 1-6 or a catalyst according to claim 7 or 8 in a chemical reaction.



## INTERNATIONAL SEARCH REPORT

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Intern ...onal Application No PCT/NL 99/00676

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B01J35/02 B01J21/04

According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 7-B01J

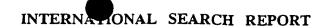
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

| C. DOCUM   | C. DOCUMENTS CONSIDERED TO BE RELEVANT  |                       |  |  |  |
|------------|---|-----------------------|--|--|--|
| Category 3 | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |  |  |  |
| X          | EP 0 008 424 A (BASF AG) 5 March 1980 (1980-03-05) claims 1,2 page 3, line 5 -page 5, line 7 example 1 figures 1,2                                  | 1,4,5,<br>7-9         |  |  |  |
| A          | DE 33 15 105 A (LEUNA WERKE VEB) 17 November 1983 (1983-11-17) the whole document   | 1,4-9                 |  |  |  |
| A .        | WO 92 05870 A (MONSANTO CO) 16 April 1992 (1992-04-16) claims 1,3,4,10-12 page 16, line 34 -page 17, line 38 page 31; table 1 figures 5A,5B,11A,11B | 1-3,7-9               |  |  |  |

| X Further documents are listed in the continuation of box C.   | X Patent family members are listed in annex.  |  |  |  |
|--|---|--|--|--|
| <ul> <li>Special categories of cited documents:</li> <li>"A" document defining the general state of the art which is not considered to be of particular relevance</li> <li>"E" earlier document but published on or after the international filling date</li> <li>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</li> <li>"O" document referring to an oral disclosure, use, exhibition or other means</li> <li>"P" document published prior to the international filing date but later than the priority date claimed</li> </ul> | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  "&" document member of the same patent family |  |  |  |
| Date of the actual completion of the international search  31 January 2000   | Date of mailing of the international search report $09/02/2000$   |  |  |  |
| Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2  NL - 2280 HV Rijswijk  Tel. (+31-70) 340-2040, Tx. 31 651 epo ni,  Fax: (+31-70) 340-3016   | Authorized officer Zuurdeeg, B  |  |  |  |

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Intern. Jonal Application No PCT/NL 99/00676

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|------------------------|--|-----------------------|
| C.(Continu<br>Category | ation) DOCUMENTS CONSIDERED TO BE RELEVANT  Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|                        |  | Total to Statin 10.   |
| A                      | EP 0 020 963 A (BASF AG) 7 January 1981 (1981-01-07) page 3, line 30 -page 5, line 29 claims 1,2 example                       | 1-3,6-9               |
| A                      | EP 0 004 079 A (HOECHST AG) 19 September 1979 (1979-09-19) claims 1,2 figures 1-6 page 3, line 32 -page 5, line 23 example     | 1-3,5,<br>7-9         |
| 4                      | EP 0 342 759 A (SHELL INT RESEARCH) 23 November 1989 (1989-11-23)  |                       |
|                        |  |                       |
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|                        |  |                       |
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Information on patent family members

Intern .Jnal Application No PCT/NL 99/00676

| Patent document<br>cited in search report |         |   | Publication date |  | Patent family member(s)   | Publication date   |
|---|---------|---|------------------|--|---|--|
| EP  | 0008424 | Α | 05-03-1980       | DE   | 2837018 A   | 06-03-1980   |
| DE  | 3315105 | A | 17-11-1983       | DD<br>BG<br>SU   | 218736 A<br>47826 A<br>1321460 A  | 13-02-1985<br>15-10-1990<br>07-07-1987   |
| WO  | 9205870 | A | 16-04-1992       | AT<br>AU<br>CA<br>CN<br>CZ<br>DE<br>EP<br>HR<br>JP<br>MX<br>NZ<br>US | 125467 T 649748 B 8859591 A 2091767 A 1061352 A,B 9300551 A 69111612 D 69111612 T 0552287 A 920509 A 6501645 T 9101444 A 240082 A 5168090 A | 15-08-1995<br>02-06-1994<br>28-04-1992<br>05-04-1992<br>27-05-1992<br>19-01-1994<br>31-08-1995<br>25-01-1996<br>28-07-1993<br>31-08-1994<br>24-02-1994<br>05-06-1992<br>26-05-1993<br>01-12-1992 |
| EP  | 0020963 | A | 07-01-1981       | DE<br>DK   | 2922116 A<br>233280 A   | 11-12-1980<br>01-12-1980   |
| EP  | 0004079 | A | 19-09-1979       | DE<br>CA<br>JP<br>US<br>US   | 2811115 A<br>1122959 A<br>54128490 A<br>4370261 A<br>4370492 A  | 27-09-1979<br>04-05-1982<br>05-10-1979<br>25-01-1983<br>25-01-1983   |
| EP  | 0342759 | A | 23-11-1989       | AU<br>CA<br>CN<br>DE<br>DE<br>IN<br>JP<br>NZ                         | 614136 B 3488089 A 1335809 A 1038033 A 68909106 D 68909106 T 2044055 T 892365 A 173763 A 2026642 A 229161 A                                 | 22-08-1991<br>23-11-1989<br>06-06-1995<br>20-12-1989<br>21-10-1993<br>13-01-1994<br>01-01-1994<br>20-11-1989<br>09-07-1994<br>29-01-1990<br>26-04-1991   |